

namely, that a 5 per cent sodium hydroxide solution was employed in effecting hydrolysis; likewise, in the fourth series, where two 30-cc. and one 20-cc. portions of chloroform were used in the recovery of phenacetin.

Series 5 and 6 involve a commercial preparation in tablet form alleged to contain 2.5 grains (0.1620 g.) each of phenacetin and salol.

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THE PRODUCTION, BOTANICAL COMPOSITION AND VOLATILE OIL STRENGTH OF AMERICAN WILD MUSTARD SEED

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The term "Wild Mustard," although regarded by botanists as being synonymous with charlock (*Brassica arvensis*), is applied by the trade to variable mixtures of charlock with brown mustard (*Brassica juncea*). Charlock is one of the most troublesome weeds in the grain and flax fields of the Northwest. Notwithstanding the means employed for its eradication by both state authorities and farmers, many of the fields of the Dakotas, Minnesota and adjoining states are masses of yellow during the flowering season and the threshed grain and flaxseed are contaminated with wild mustard seed. Other plants belonging to the mustard family occur with the charlock but most of these, such as pepper grass (*Lepidium virginicum*), shepherd's purse (*Capsella bursa-pastoris*) and false flax (*Camelina sativa*), do not have globular seeds. The notable exception is brown mustard, the seeds of which resemble those of charlock in size and almost invariably occur in greater or less amount mixed with the latter in the so-called "Wild Mustard" separated at the elevators, flour mills, malt houses, seed warehouses, and linseed works.

The total production of so-called wild mustard is very large. Samples of wheat examined in a single day under the direction of Mr. G. H. Tunnell, Chief State Grain Inspector, Minneapolis, in the presence of one of the writers, contained as high as 2.15 per cent of wild mustard and much larger amounts were stated to be not uncommon. A sample representing the total screenings output of one of the large Minneapolis mills contained 11.04 per cent of wild mustard of which 10.74 per cent was charlock and 0.30 per cent brown mustard.

Assuming an average of only 0.1 per cent for the entire spring wheat crop of 1913, the grand total would be about 180 carloads of 40 tons each. This estimate, which is doubtless much too low for the wheat crop, does not include the wild mustard separated from barley, rye and linseed, and that produced in adjoining provinces of Canada.

A grain merchant thoroughly acquainted with the situation reported that upward of 100 carloads annually were separated from grain in Minneapolis alone and another trade authority stated that this estimate was much too low. Large quantities are said to be shipped to Europe.

SEPARATION OF WILD MUSTARD FROM GRAIN AND OTHER SEEDS

Screenings consisting of foreign seeds, chaff and other impurities are first separated into different grades by means of sieves and air currents. The grade containing the wild mustard seed includes other seeds, notably green fox tail (*Chaetochloa viridis*), and seed fragments of about the same size which are removed by ingenious machines, depending on the fact that these impurities do not roll with as great ease on an inclined surface as the round seed of wild mustard.

Two types of power separators, namely, the belt and the disk machines, are in common use and recently a spiral "extractor" containing no moving parts has been placed on the market.

THE BELT MACHINE consists of a broad belt running on two horizontal pulleys, one of which is higher than the other so that the upper surface of the belt forms an inclined plane moving slowly forward toward the higher pulley. A broad but thin stream of screenings is continually delivered on the belt from a hopper. The round seeds of the wild mustard roll down the belt into a suitable receptacle while the other seeds, because of their irregular form, do not roll but are carried by the belt in the opposite direction and discharged at the upper end.

THE DISK MACHINE employs several metal disks sloping slightly toward the center and revolving on the same vertical shaft. The screenings are delivered at a point near the edge of each disk. As the disk turns, the wild mustard seeds roll toward the center where they enter a chute, while the other seeds are carried around and are brushed off near the feeding point.

THE SPIRAL "EXTRACTOR" consists of a stationary spiral with several turns made up of three chutes into which the screenings are fed through a hopper. In their passage downward, the wild mustard seeds acquire sufficient velocity to jump outward into the middle and finally the outer chute from which in turn they pass into a hopper outlet, while the other seeds and impurities remain in either the middle or inner chute and emerge through two other outlets.

DISTINCTION BETWEEN CHARLOCK AND BROWN MUSTARD

The important distinctions between the two seeds which make up the wild mustard of commerce are as follows:

1—Brown mustard is an escaped plant which in Russia is cultivated for its seed; charlock is an introduced weed regarded everywhere as a pest.

2—Brown mustard is dark brown and under a lens shows distinct reticulations; charlock varies from dark brown to nearly black and under a lens is finely granular but not reticulated.

3—The hulls of brown mustard do not respond to the chloral hydrate test; the hulls of charlock gently heated with this reagent become carmine-red.¹

4—Brown mustard, like black mustard (*Brassica nigra*), contains potassium myronate, which on treatment with water, owing to the action of the myrosin, splits up with the formation of volatile mustard oil;

¹ Waage, *Ber. Pharm. Ges.*, 1893, p. 153; Winton, *Orig. Com. 8th Intern. Cong. Appl. Chem.*, 26 (1912), 409.

charlock, as shown by Dircks,¹ Jorgensen² and ourselves, does not contain substances which yield any considerable amount of volatile oil by this treatment.

In addition there are histological differences which need not be considered here.

The distinction based on the formation of volatile oil is of great practical importance as it affects not only the flavor but the value of the seed for plasters and other medicinal preparations. White mustard (*Brassica alba*) does not yield volatile oil with water, but it does contain sinalbin and possibly other substances to which indirectly it owes its agreeable pungency, whereas charlock, although somewhat pungent, is recognized by the trade to be of inferior flavor. Cognizance of the inferiority of charlock has been taken by authorities on both foods and drugs. It is not recognized by the U. S. Pharmacopoeia or in the food standards; furthermore, the U. S. Government has issued a decision³ requiring that it and its products be designated as charlock and not as mustard.

UTILIZATION OF WILD MUSTARD

The removal of foreign seeds from grain is obviously necessary in order to secure a high-grade product. The further separation of wild mustard from the screenings is also desirable as it is distasteful to farm animals. Commercial wild mustard thus obtained is properly utilized for the production of oil which is valuable for technical use if not for human food. It remains to be determined what shall be done with the oil cake. Hitherto this has been added to mustard

The percentage composition of a sample of wild mustard cake consisting largely of charlock follows:

Moisture	Ash	Protein (N $\times$ 6.25)	Crude fiber	N-free extract	Fat	Total
9.20	5.42	31.19	10.44	26.93	16.82	100.00
Nitrogen	Phosphoric acid	Potash	Volatile mustard oil			
4.99	1.54	1.02	0.23			

This analysis shows the product to be nearly equal in fertilizing value to castor pomace of average quality.

EXAMINATION OF SAMPLES OF COMMERCIAL WILD MUSTARD SEED

Early in the winter of 1913 one of the writers visited a number of mills, elevators, malt houses and seed warehouses in Minnesota, Wisconsin and Illinois, where wild mustard is separated from grain and other seed, and took samples for examination. Samples of pure seed of the four common species, namely, white, black, and brown mustard, and charlock, were kindly furnished for comparison by Professors Freeman and Oswald, of The Farm School, University of Minnesota.

Determinations of the percentages of charlock, brown mustard and foreign seeds were made on the commercial samples by picking out the different seeds under a lens and weighing. The results were corrected for the foreign seeds, and determinations of volatile oil were made by Roeser's method¹ on the mixture of charlock and brown mustard obtained in the separations. The results appear in Table I. It appears from these data that while brown mustard yields a good amount of volatile oil, charlock, like

TABLE I—BOTANICAL COMPOSITION AND VOLATILE OIL STRENGTH OF CHARLOCK, MUSTARDS, AND COMMERCIAL WILD MUSTARD

KIND OF SAMPLE	SOURCE OF SAMPLE	Kind of separator	Per cent analysis of samples as separated			Per cent analysis calculated free of foreign seeds			Per cent volatile oil calculated from botanical analysis
			Charlock	Brown mustard	Foreign seeds	Charlock	Brown mustard	Volatile mustard oil	
Pure charlock (<i>B. arvensis</i>)	Commercial wild mustard		100	0	0	100	0	0.15	
Pure charlock (<i>B. arvensis</i>)			100	0	0	100	0	0.25	
Pure brown mustard (<i>B. juncea</i>)			0	100	0	0	100	2.89	
Pure black mustard (<i>B. nigra</i>)								4.62	
Pure white mustard (<i>B. alba</i>)	Grown at the Farm School, University of Minnesota							0.16	
COMMERCIAL WILD MUSTARD:									
Elevator, Devil's Lake, N. D.	Flax		0.5	99.5	0	0.5	99.5	2.42	
Elevator, Milwaukee, Wis.	Barley	Disk	90.5	4.7	4.8	95.1	4.9	0.24	0.26
Malt house, Minneapolis	Barley	Disk	88.0	10.7	1.3	89.1	10.9	0.38	0.40
Flour mill, Minneapolis	Wheat	Belt	85.2	9.0	5.8	90.4	9.6	0.36	0.38
Flour mill, Minneapolis	Wheat	Belt	82.1	12.9	5.0	86.4	13.6	0.41	0.46
Flour mill, Minneapolis	Wheat	Belt	87.5	8.5	4.0	91.2	8.8	0.33	0.35
Flour mill, Minneapolis	Wheat	Belt	75.7	18.2	6.1	80.6	19.4	0.57	0.60
Flour mill, Minneapolis	Wheat	Belt	47.8	35.8	16.4	57.3	42.7	1.14	1.13
Flour mill, Minneapolis	Wheat	Belt	57.3	27.6	15.1	67.5	32.5	0.94	0.89
Flour mill, Minneapolis	Wheat	Belt	73.5	24.5	2.0	75.0	25.0	0.91	0.72
Flour mill, Chicago	Wheat	Disk	86.6	2.5	10.9	97.2	2.8	0.19	0.21
Seed house, Minneapolis			89.0	9.0	2.0	90.8	9.2	0.43	0.36
Seed house, Chicago			66.2	28.5	5.3	69.9	30.1	0.91	0.83
Seed house, Chicago			87.4	11.8	0.8	88.1	11.9	0.47	0.42

flour and prepared mustard, but for reasons already stated, such products are considered adulterated if not properly labeled as to the presence of charlock.

A rational use for cake containing a considerable amount of charlock would appear to be as a nitrogenous fertilizer for tobacco. Castor pomace, the residue from the manufacture of castor oil, which, owing to its poisonous nature cannot be fed to cattle, is used as a fertilizer, but the supply is limited and large quantities of cottonseed meal make up the deficiency. If charlock cake were found suitable for this purpose, a corresponding amount of cottonseed meal could be released for feeding, for which purpose it is well adapted.

white mustard, is practically valueless in this respect. Samples of brown mustard and charlock grown at the Minnesota Farm School gave 2.89 and 0.25 per cent and others picked out from commercial wild mustard, 2.42 and 0.15 per cent of volatile oil respectively. The somewhat lower amounts in the latter case are possibly due to the conditions of growth in the grain fields as compared with those on the experimental farms where the plants had undisputed claim on the soil and light and the seed was harvested when ripe. The high percentage of volatile oil in the black mustard should be noted.

The relative amount of brown mustard and charlock in the samples of commercial wild mustard was ex-

¹ Landw. Versuchs., 28 (1883), 179.

² Nyt Tidskrift for Fysik og Kemi, 3, 91.

³ Food Inspection Decision No. 137.

¹ Jour. Pharm. Chim., [6] 15 (1902), 361; Leach, "Food Inspection and Analysis," New York, 1914, p. 457.

ceedingly variable. In all the samples from grain the amount of charlock was invariably greater than that of brown mustard, ranging from 95.1 to 57.3 per cent as calculated to the pure wild mustard after correcting for foreign seed and impurities. A single sample of wild mustard from flax seed was almost absolutely pure brown mustard.

It should further be noted that the volatile oil obtained in the commercial samples was approximately proportional to the percentage of brown mustard present. This relation is so uniform that the volatile oil can be calculated from the botanical analysis with practically as great accuracy as by direct determination. For this purpose, the following formula based on the determinations made on the samples of the seeds separated from commercial wild mustard may be used:

$$V = 2.42 B + 0.15 C$$

in which V is the percentage of volatile oil, B is the percentage of brown mustard and C is the percentage of charlock. A comparison of the percentages of volatile oil found by analysis and as calculated by this formula in the samples of commercial wild mustard seed cleaned free of foreign seeds is given in the last column of Table I.

It can hardly be expected that a formula based on determinations made on only one sample each of brown mustard and charlock will give strictly accurate results in all cases, but the figures obtained on the samples examined by us show remarkable agreement and suggest further work both on wild mustard seed and the cake.

Determinations of volatile mustard oil in mustard flour may prove useful in estimating the approximate amount of charlock present as an adulterant provided this determination is supplemented by careful microscopic examination. It should not be forgotten, however, that in the presence of white mustard, which, like charlock, yields practically no volatile oil, or of black mustard, which may contain more than the brown, it would be impossible to arrive at a correct estimate from the volatile oil alone. Of special value in the case of such mixtures is an estimate based on the amount of hulls reacting with acid chloral hydrate solution.

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THE DETERMINATION OF SULFATES IN SOILS

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In undertaking a study of the process of sulfonation or sulfur oxidation in soils, the first problem which arose was the selection of an accurate method for the determination of the sulfates. Wiley gives directions for the determination without comment as to any difficulties to be met with. As he describes it, the method merely calls for treatment of the soil with cold, dilute hydrochloric acid, filtration and precipitation with barium chloride and weighing the sulfate formed. In the work of the few investigators who have made observations on the formation of sulfates in soils, the method of extraction of the sulfates is usually not mentioned and when the point is considered worthy of notice, the rather indefinite statement is made that the soil

is treated with dilute hydrochloric acid. Is it important that a certain strength of acid should be employed in order to accomplish complete extraction? What should be the length of time of contact with the acid? These are questions which immediately arise and the experiments reported here were carried out to answer them and to develop a method which would permit of an accurate estimation of sulfates as such in the soil.

EXPERIMENTAL

In the first experiments, therefore, 100-gram quantities of soil were shaken in the shaking machine for two hours with 200 cc. of 0.5, 1.0, 2.0, 5.0 and 10.0 per cent hydrochloric acid and with 200 cc. of water. A comparative series was run under exactly the same conditions except that 2 cc. of a 5 per cent solution of magnesium sulfate were added to each 100-gram quantity of soil. The amount of sulfate extracted in each case from the soil itself was thus determined and subtracting this figure from the total amount of sulfate obtained, the extraction from the magnesium sulfate added was found. The sulfates were determined in these cases by the usual gravimetric method using barium chloride. The results of these tests appear in Table I.

TABLE I—CONCENTRATIONS OF ACID VARIED

Lab. No.	Per cent HCl used	Grams $MgSO_4$ added	Milligrams S extracted as Sulfates		Milligrams sulfur added from $MgSO_4$		Not extr. from $MgSO_4$ added	
			Duplicates	Av.	SO_4 from $MgSO_4$	Added as $MgSO_4$	from $MgSO_4$	
1, 2....	0.5	None	1.18	0.77	0.97	24.14	26.63	2.49
3, 4....	0.5	0.1	24.19	26.04	25.11			
5, 6....	1.0	None	1.10	1.76	1.43	23.73	26.63	2.90
7, 8....	1.0	0.1	23.94	26.38	25.16			
9, 10....	2.0	None	1.74	0.91	1.32	23.15	26.63	3.48
11, 12....	2.0	0.1	24.47	24.47	24.47			
13, 14....	5.0	None	2.04	1.44	1.74	29.45	26.63	Excess
15, 16....	5.0	0.1	30.92	31.46	31.19			
17, 18....	10.0	None	1.10	1.40	1.25	39.70	26.63	Excess
19, 20....	10.0	0.1	36.52	45.38	40.95			
21, 22....	Water	None	4.00	4.12	4.06	26.46	26.63	0.17
23, 24....	Water	0.1	30.70	30.34	30.52			

Upon examination of these results it is found that treating a soil with hydrochloric acid in any of the strengths used did not permit of the determination of sulfates known to be contained in the soil. The weakest acid used allowed only a partial recovery of the sulfate added and as the concentration was increased up to 2.0 per cent acid the recovery became gradually smaller. With 5 and 10 per cent acid, however, the recovery was entirely too high, that with the 10 per cent acid being greater than that with the 5 per cent.

It is evident from these tests that there are some disturbing factors which prevent the extraction of sulfates from soils by hydrochloric acid. Van Bemmel¹ observed that with hydrochloric acid much humus substance and iron oxide were dissolved and that these interfered with the determination of sulfates, causing low results. He found further that it was impossible to remove these substances without obtaining high results because of the oxidation of the sulfur in the dissolved organic matter.

Furthermore, with 5 or 10 per cent acid there is undoubtedly some solution of silica and this would make the results too high, as they have been shown to be.

It may be concluded, therefore, from these results

¹ Landw. Vers. Sta., 37, 284.